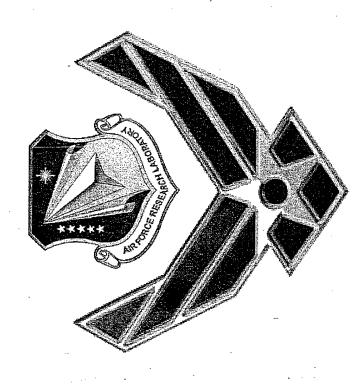
Form Approved REPORT DOCUMENTATION PAGE OMB No. 0704-0188 Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS. 3. DATES COVERED (From - To) 1. REPORT DATE (DD-MM-YYYY) 2. REPORT TYPE Technical Viewgraph Presentation 23-09-2003 5a. CONTRACT NUMBER 4. TITLE AND SUBTITLE F04611-99-C-0025 **5b. GRANT NUMBER Polynitrogen Chemistry 5c. PROGRAM ELEMENT NUMBER 5d. PROJECT NUMBER** 6. AUTHOR(S) DARP 5e. TASK NUMBER Karl O. Christe (ERC) A205 5f. WORK UNIT NUMBER 8. PERFORMING ORGANIZATION REPORT 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NUMBER ERC, Inc. 10 East Saturn Blvd. Edwards AFB CA 93524-7680 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) 10. SPONSOR/MONITOR'S ACRONYM(S) Air Force Research Laboratory (AFMC) 11. SPONSOR/MONITOR'S AFRL/PRS NUMBER(S) 5 Pollux Drive Edwards AFB CA 93524-7048 AFRL-PR-ED-VG-2003-240 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited. 13. SUPPLEMENTARY NOTES For presentation at the 2nd Advanced Energetics Technology Exchange taking place at the Aberdeen Proving Grounds, MD, from 22-26 September 2003. 14. ABSTRACT

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15. SUBJECT TERMS

POLYNITROGEN CHEMISTRY



Karl Christe

ERC, Inc and Propellants Branch,
Propulsion Directorate,
Air Force Research Laboratory,
Edwards AFB,
and
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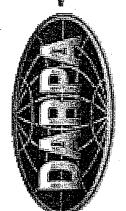


















Dr. William Wilson Dr. Robert Corley Dr. Karl Christe Dr. Ashwani Vij Dr. Jerry Boatz

Thorsten Schroer Dr. Stefan Schneider Dr. Ross Wagner Ms. Vandana Vij Dr. Ralf Haiges

Dr. Heather Netzloff (ISU) Dr. Mark Gordon (ISU) Dr. David Dixon (PNL) Dr. David Feller (PNL) Dr. Don Jenkins (UW





Program Objectives

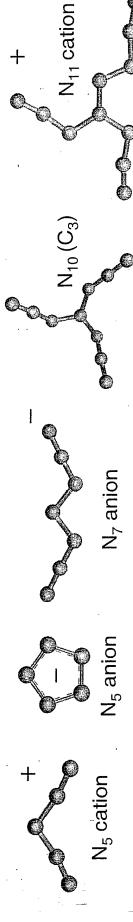




novel, highly energetic polynitrogen compounds Discover, synthesize, characterize, and scale-up

Technical Approach:

- Exploit synergism between theory and synthesis
- Use calculations to identify the most promising candidates and predict their properties
- Use experimental expertise to design synthesis approaches, prepare novel compounds, and characterize products



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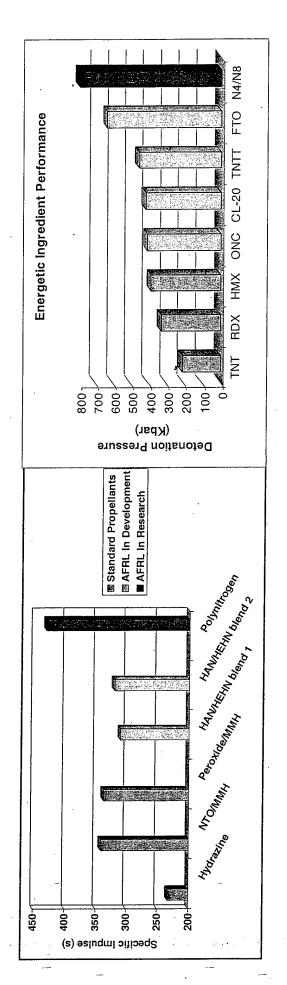


Monopropellants and Explosives Performance of Polynitrogen as





The performance of polynitrogens as monopropellants would dwarf that of hydrazine, and would greatly exceed even bipropellants



Polynitrogens Would also have great potential as high-performance explosives, with performance 2-3 times that of current materials



Previous Accomplishments



- Discovered N₅⁺, the first new stable polynitrogen species in more than 100 years and only the second known stable homonuclear polynitrogen species
- Prepared and characterized $N_5^+AsF_6^-$, $N_5^+SbF_6^-$, $N_5^+Sb_2^-F_{11}^-$, $N_5^+B(CF_3)_4^-$, N_5 +SnF $_5$ -, and $(N_5$ + $)_2$ SnF $_6$ 2-
- Scaled up N₅+SbF₆ production to 5 g level
- Obtained experimental evidence for instability of $N_5^+N_3^-$, $N_5^+NO_3^-$, and $N_5^+CIO_4^-$
- Prepared and characterized the N₃NOF+ cation
- Experimentally detected the pentazolate anion, cyclo-N5-, by electrospray negative ion mass spectroscopy

S



Recent Results



- Synthesis of N₅+HF₂·nHF, N₅+PF₆·, N₅+BF₄·, and N₅+[P(N₃)₆]-
- Reactions of NF_4^+ and $N_2F_3^+$ with HN_3^-
- FN₅
- Bulk Synthesis of N₅-
- Can N_5 + N_3 and N_5 + N_5 exist?
- Polyazido compounds



Synthesis of N5+HF2-nHF



ullet Original plan was the metathetical synthesis of $N_5^+N(CF_3)_2^-$

$$N_5$$
+SbF₆ + Cs+N(CF₃)₂ - HF, -78 C CsSbF₆ + N_5 +N(CF₃)₂

- Filtered off CsSbF₆ and pumped off all volatiles at -64 C
- Obtained clear colorless liquid, Raman of which showed only bands due to N_{5}^{+}
- Actual reactions

$$N_5$$
+SbF₆ + Cs+N(CF₃)₂ - CsSbF₆ + N_5 +N(CF₃)₂

$$N_5^+N(CF_3)_2^- + (n+2)HF \longrightarrow N_5^+HF_2^-(nHF) + HN(CF_3)_2$$

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$$N_5$$
+ HF_2 - + A ------- N_5 + AF - + HI

Any Lewis acid that has a higher F- affinity than HF (45 kcal/mol) should be able to displace HF

Principle was successfully demonstrated for

 BF_3 (82 kcal/mol) and PF_5 (94 kcal/mol)

and $\rm N_5{}^+BF_4{}^-$ and $\rm N_5{}^+PF_6{}^-$ were isolated as stable solids and characterized

 ∞

*Attempted Syntheses of N_x+ Species (x = 11, 13)





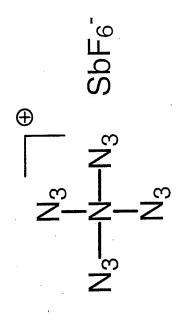
Desired product (N₃)₂NN(N₃)SbF₆

 $N_2F_3SbF_6 + 3HN_3 ---$

 SbF_6

Desired product N(N₃)₄SbF₆

-78°C to -20°C $\mathsf{NF_4SbF_6} + \mathsf{4HN_3} -$





Reaction of NF₄⁺ with HN₃





Reaction of NF₄⁺

$$HF/-78 C$$

 $NF_4SbF_6 + HN_3 \longrightarrow NF_3 + HF + FN_3 + SbF_5$

$$2 \text{ FN}_3 \longrightarrow 2 \text{ N}_2 + trans-\text{N}_2\text{F}_2$$

$$HN_3 + HF + SbF_5 \longrightarrow H_2N_3SbF_6$$

3 trans-
$$N_2F_2 \longrightarrow 2 N_2 + 2 NF_3$$

 $^{\prime}$ NF $_{4}^{+}$ acts as a fluorinating agent, fluorinating HN $_{3}$ to FN $_{3}$

10



Reaction of N₂F₃+ with HN₃



Reaction of F₂NNF⁺

$$F_2NNF^+SbF_{6^-} + HN_3 \xrightarrow{HF/-78 \text{ C}} [F_2NNN_3^+SbF_{6^-}] + HF$$
 $[F_2NNN_3^+SbF_{6^-}] \xrightarrow{HF/-78 \text{ C}} [F_2NNN^+SbF_{6^-}] + N_2$

$$[F_2NNN^+SbF_6^-]$$
 ——— $[F_2N^+SbF_6^-]$ + N_2

$$[F_2N+SbF_6]$$
 — $NF_3 + SbF_5$

$$HN_3 + HF + SbF_5 \longrightarrow H_2N_3 + SbF_6$$

substitution mechanism over an oxidation reaction with N_2F_2 formation The absence of N₂F+SbF₆ or N₅+SbF₆ in the product favors this









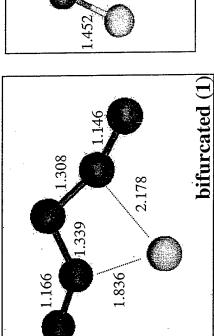
- Controlled decomposition of $(N_5^+)_2 SnF_6^{-2}$ to $N_5^+ SnF_5^-$ and "FN₅" allowed us to search for FN₅ by dynamic FT-IR spectroscopy
- Observed only FN₃ and its decomposition products (N₂F₂ and NF₃)
- Theoretical study was carried out showing six stable isomers differing by about 6 (MP2) and 10 (CCSD(T)) kcal/mol in energy
- Intrinsic reaction coordinate and dynamic reaction path calculations were used to study the isomerization and decomposition of FN₅
- Based on a Rice-Ramsperger-Kassel-Marcus analysis, the lifetime of ${\sf FN}_5$ was estimated to be in the nanosecond range explaining our failure to observe FN $_{\scriptscriptstyle \mathrm{S}}$ experimentally

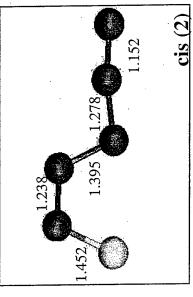


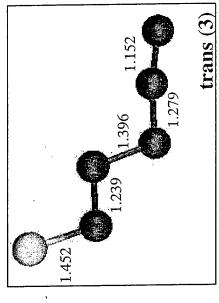
Six FN₅ Isomers (MP2/6-31++G(d,p))

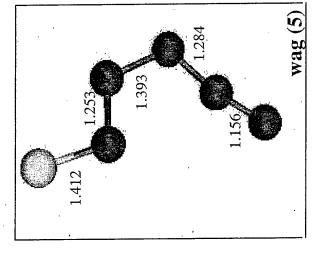


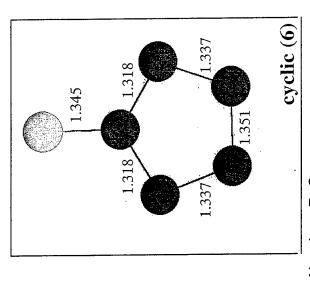












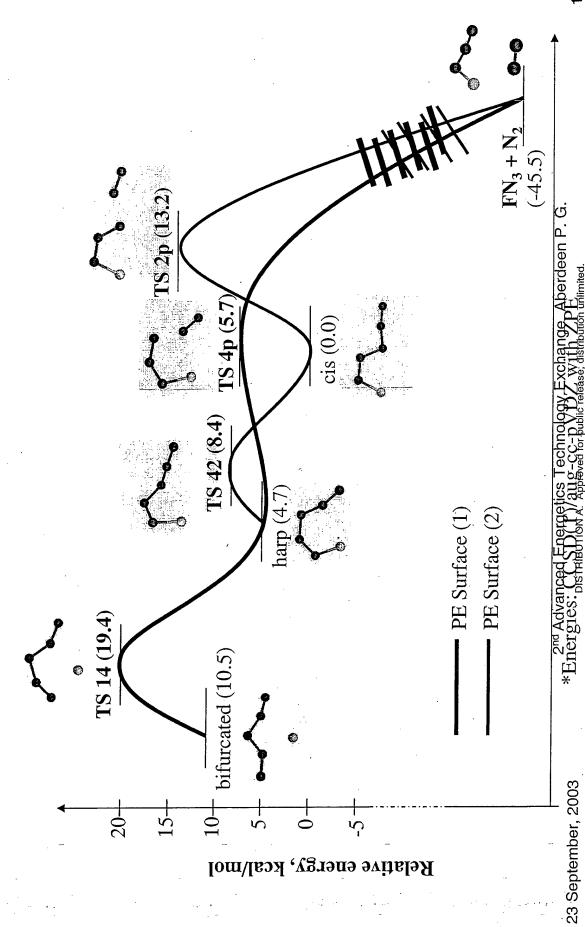
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23 September, 2003

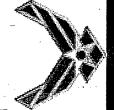
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Figure 8. Relative isomerization/decomposition PESs with FN_5 isomers (reference = *cis*-isomer)

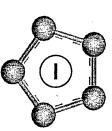






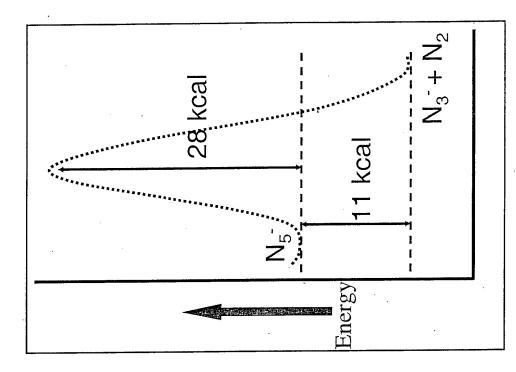
Pentazolate Anion





©—© Pentazolate anion (N₅-)

- to N₃ and N₂ is only 11 kcal/mol exothermic for decomposition, a high vertical ionization potential of 5.58 eV, and its decomposition has a 28 kcal/mol activation energy barrier and Bartlett et al) predicted that this anion Theoretical calculations (Nguyen and Ha,
- Aryl substituted pentazoles had been known for 40+ years, but all previous attempts to isolate HN_5 or N_5 had failed



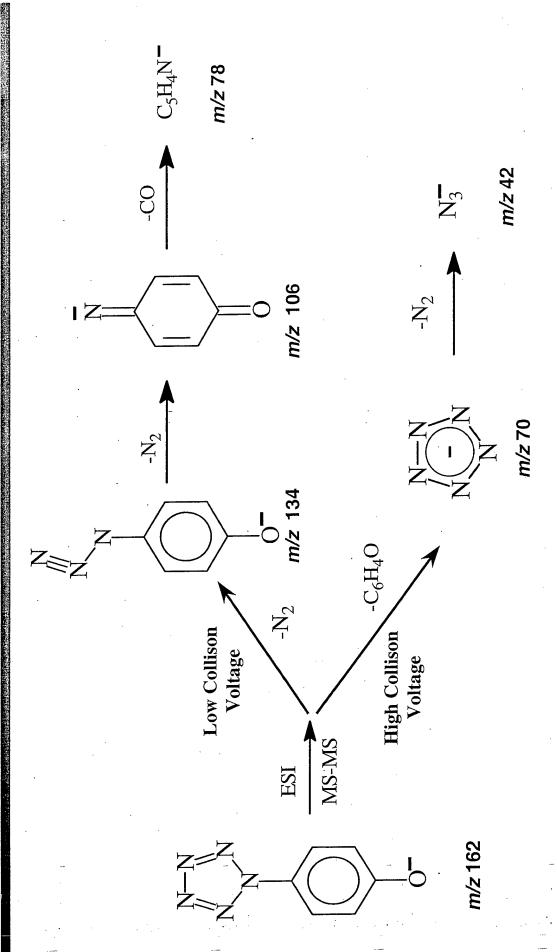
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Pentazolylphenolate (Angew. Chem. 2002,41, 3051 Identification of N₅ by ES-IMS of para-





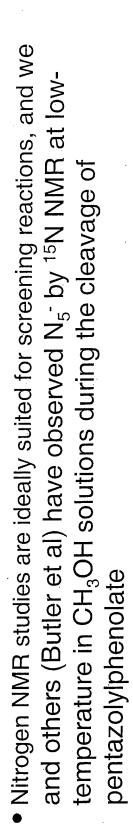


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Search for a Bulk Synthesis of N₅





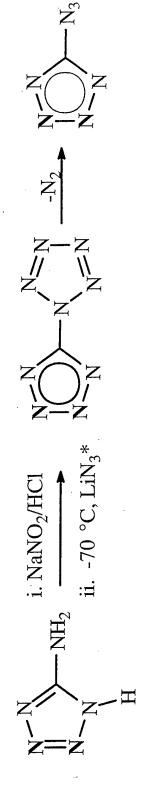
We have also demonstrated by 15N NMR that azolyl substituents are better leaving groups





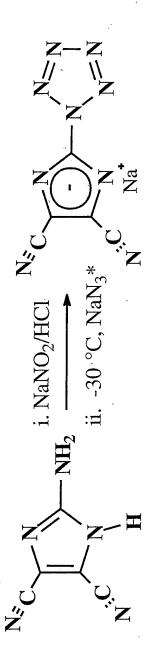
Pentazoles with Heterocyclic Substituents

pentazole ring rapidly decomposes to liberate N₂ gas. Tetrazolyl system is unstable above -70 °C and the



A. Hammerl and T. M. Klapoetke, Inorg. Chem. 2002, 41, 906-912

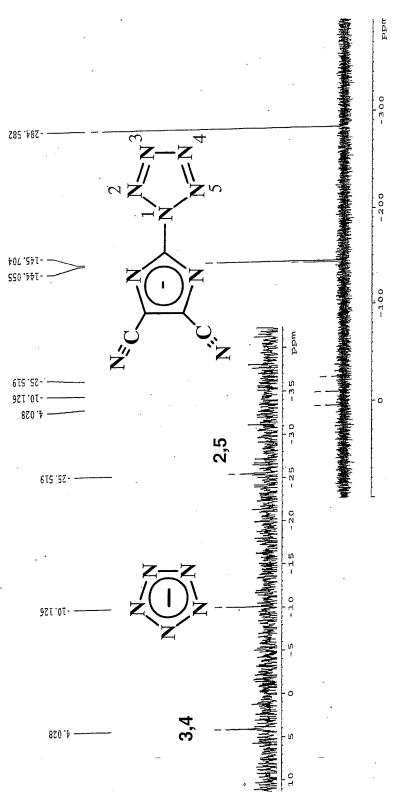
dicyanoimidazole shows higher thermal stability (-30 $^{\circ}$ C) By comparison, the pentazole derivative of 2-amino-4,5-



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15N NMR of N₅- in Solution





 $^{
ightarrow}$ ¹⁵N NMR shows a peak at -10 ppm (-30 $^{\circ}$ C), which slowly decomposes to form N $_2$ and azide ion. This peak is also observed upon adding OH- to the solution of arylpentazoles at -30 °C.

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Existence of N5+N3 and N5+N5



- Previously published stability predictions and energy density calculations adiabatic electron affinity and ionization potentials. This can cause huge for $\mathsf{N}_5{}^+\mathsf{N}_5{}^-$ and $\mathsf{N}_5{}^+\mathsf{N}_3{}^-$ are incorrect due to the use of vertical instead of
- oracketing the electron affinity of ${\sf N}_{{\sf S}^+}$ (10.52-11.48 eV) which agrees well with our calculated adiabatic value of 10.55 eV, but not with the vertical The correctness of our approach was demonstrated by experimentally value of 6.04 eV.
- We have calculated highly accurate enthalpies of formation and adiabatic electron affinities and ionization potentials for N₃, N₃-, N₅+ and N₅- from total atomization energies.
- The stability of an ionic solid is governed by the sum of the first ionization potential of the anion, the electron affinity of the cation, and the lattice energy, as shown by the following Born-Haber cycles.



Born-Haber Cycles for N5+N3 and N5+N5-







$$H \longrightarrow (N_3^{\bullet}_{(g)} + N_{2(g)}) + (N_3^{\bullet}_{(g)} + N_{2(g)})$$

 $.4 \pm 5.7$

$$N_5^+(g) + N_5^-(g)$$

 $\Delta H_{\rm L} = 134 \pm 5$

$$IP (N_5) = 47.9 \pm 2$$

EA
$$(N_5^+) = -243.3 \pm 2$$

Problem with the N₅ ions:

N₃. Because N₃ has a barrier, N₅+N₃radicals are vibrationally unstable and decompose without barrier to Both, cyclic and catenated N₅ is less unstable than N₅+N₅-

 For a salt to be stable, ΔHr must be zero or positive

$$N_5^+ N_3^-$$
(s) AH_r N_3 (g) + N_3 (g) + N_2 (g) -36.1 ± 7.5

$$\Delta H_{L} = 146 \pm 7$$

$$N_5^+(g) + N_3^-(g)$$

IP
$$(N_3^-) = 61.2$$

IP
$$(N_3) = 61.2 \pm 2$$

$$EA (N_5^+) = -243.3 \pm 2$$

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2



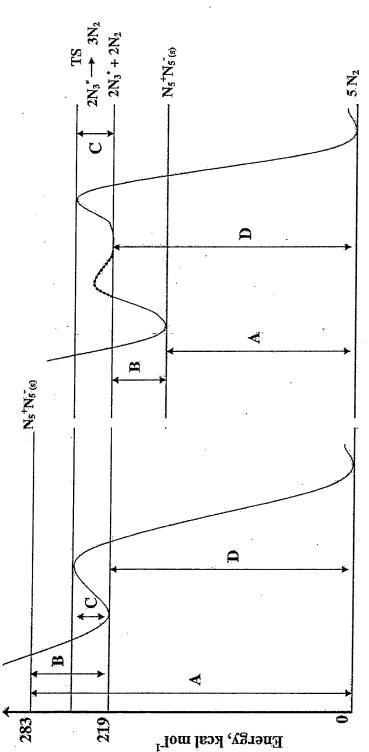
Potential energy curves for N₅+N₅-





NEGATIVE B VALUE, KINETICALLY UNSTABLE, REPRESENTS CALCD VALUES

POSITIVE B VALUE AND KINETIC STABILITY WOULD REQUIRE $\Delta H_r (N_s^+ N_{\tilde{s}'(s)}) \approx 180 \text{ kcal/mol}$



 $A = \Delta H_{\Gamma} (N_5^+ N_{5,(5)})$

 $- 2N_{3 \, (g)} + 2 N_{2 \, (g)}) = U_{L} (N_{5}^{\dagger} N_{5}^{-} g) + 2 RT + IP (N_{5 \, (g)}) - EA (N_{5 \, (g)})$ $\mathbf{B} = \Delta \mathbf{H}_{r} \cdot (\mathbf{N}_{s}^{\dagger} \mathbf{N}_{s}^{\dagger} \mathbf{s}) -$

C = Activation energy barrier for decomposition of 2N3 (g) 3N3

 $D = \Delta H_r (2N_s^{\circ})_{(g)}$ 3N₂

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Conclusions concerning the stability of N5+N5 and N5+N3





- Our results predict that $N_5^+N_3^-$ and $N_5^+N_5^-$ are unstable and decompose spontaneously with N_2 evolution.
- This conclusion was experimentally confirmed in our laboratory for

▶ Desired metathesis:

$$N_5SbF_6 + CsN_3 \xrightarrow{SO_2} N_5N_3 + CsSbF_6 -64^{\circ}C$$

Obtained products:

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Polyazide Chemistry



- Complex azides have great potential for energetic high-nitrogen ingredients and as potential counter-ions for N5+
- Typical examples of compounds previously prepared by us:

$$C(N_3)_3^+CIO_4^-, C(N_3)_3^+N(NO_2)_2^-, and C(N_3)_3^+NO_3^-$$

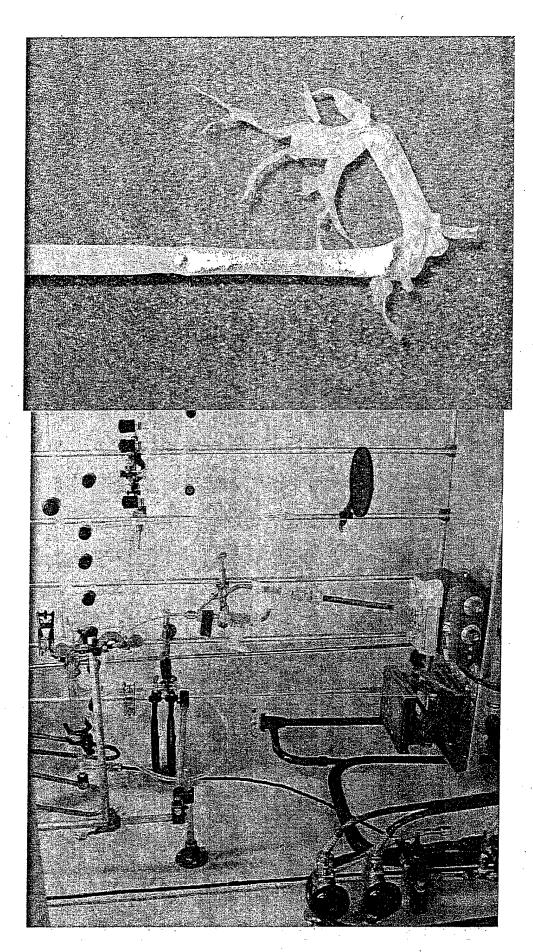
Compounds studied under this program include

$$As(N_3)_3$$
, $Sb(N_3)_3$, $As(N_3)_5$, $Sb(N_3)_5$, $As(N_3)_6$, $Sb(N_3)_6$, $Te(N_3)_6$, $Te($

- Most of these compounds are very sensitive, but some can be safely handled, particularly when combined with large counter-ions
- fluorides or chlorides with $(CH_3)_3SiN_3$ in suitable solvents, such Their synthesis generally involves the reactions of the corresponding

How much damage can 1/2 mmol of $N_5^+[P(N_3)_6]$ cause ?



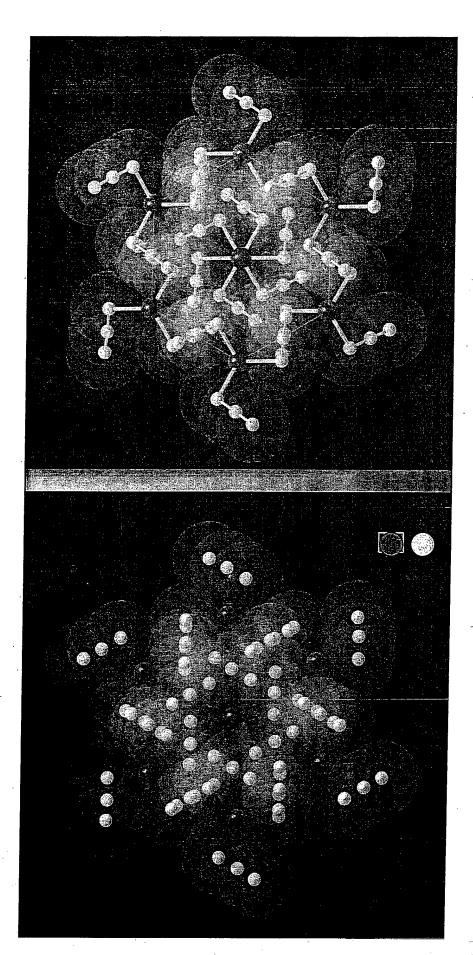


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Normal Polyazides





Covalent azides are normally strongly bent with M-N-N angles of **about 120°, as shown here for Sb(N₃)**2nd Advanced Energetics Technology Exchange, Aberdeen P. G.

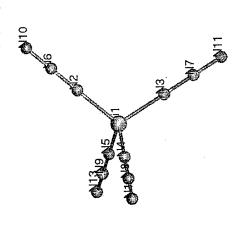
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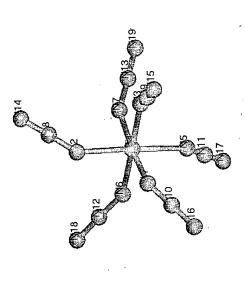


Novel type of covalent azides with linear M-N-N bonds



- Based on quantum chemical calculations, Gagliardi and Pyykkoe have $\mathsf{Hf}(\mathsf{N}_3)_4$, and $\mathsf{Th}(\mathsf{N}_3)_4$ a novel type of bonding involving linear M-N-N bonds. recently predicted, (*Inorg. Chem.* **2003**, 42, 3074), for $Ti(N_3)_4$, $Zr(N_3)_4$,
- Based on our calculations, we also expect that the $Ti(N_3)_6^{2-}$ anion possesses We have confirmed these calculations for $Ti(N_3)_4$ and also predict that other azides, such as $Fe(N_3)_2$ (Melanie Teichert), can form linear M-N-N bonds. the usual bent M-N-N bonds.





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Synthesis and Characterization of Ti(N₃)₄ &



Synthesis

TiHal₄ + exc. TMSN₃
$$\rightarrow$$
 Ti(N₃)₄ + 4 TMSCI

Properties

28

Raman spectrum and comparison with calculated spectra suggest that CN might be higher than 4 and Ti-N-N angle might be bent

 $[\]nearrow$ Need a gas-phase structure of free Ti(N₃)₄



Possible explanations for linear M-N-N bonds

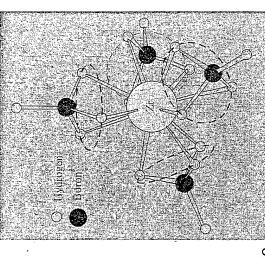




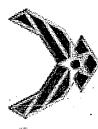
- Gagliardi and Pyykkoe invoke conjugation.
- distances are relatively long and are similar to single bonds. Also, the ${\sf N_g} ext{-}{\sf N_v}$ bonds are quite short, and the Ti-N-N bonds in ${\rm Ti}({\rm N}_3)_6^{2^-}$ are strongly bent. We prefer the following interpretation because the calculated Ti-N bond

which can act as a tridentate ligand and, in a tetrahedron, can perfectly \nearrow The N_{α} atom of the $-N_{3}$ ligand has three free valence electron pairs overlap with three of the lobes of the Ti 3d-orbitals. This scheme is analogous to the structure of $Zr(BH_4)_4$ which

possesses 4 trihapto BH₄ groups. In the usual covalent azides, the azide ligands utilize only one electron pair of the N_{α} atom for the bonding, and the presence of two additional, sterically active free valence electron pairs results in a pyramidal configuration with an M-N-N angle of about 120 °.



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Conclusions



- The novel N_5 +HF $_2$ salt was prepared and serves as a useful reagent for the preparation of other N₅+ salts.
- The reactions of NF_4^+ and $N_2F_3^+$ with HN_3 were studied. While NF_4^+ acted only as a fluorinating agent, one F of $N_2F_3^+$ was replaced by an azido group, but the substitution product was unstable and underwent rapid decomposition.
- experimentally and computationally. It was shown that the life-time of ${\sf FN}_5$ is very short and that under our reaction conditions only the expected The decomposition of complex fluoro salts of N₅+ was studied both decomposition products can be observed.
- In pursuit of a bulk synthesis for $N_{\rm 5}$ salts, it was shown that the $N_{\rm 5}$ anion can be prepared in solution and be observed by 15N NMR.
- Reliable thermodynamic calculations were carried out for N_5 + N_5 and N_5 + N_3 . It is shown that the previous use of vertical instead of adiabatic potentials led to very large errors and erroneous conclusions.
- Numerous polyazido compounds of P, As, Sb, Te, B, and Ti were prepared and
- ullet $N_5^+[P(N_3)_6]^-$ was successfully prepared and characterized by low-temp. Raman. 2nd Advanced Energetics Technology Exchange, Aberdeen P. G.